

B10

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 January 2001 (18.01.2001)

PCT

(10) International Publication Number  
WO 01/04388 A2

(51) International Patent Classification<sup>7</sup>: C30B 15/00,  
29/06

AZAROWSKI, Sean, M.: 107 West Glenwood Drive,  
Nashua, NH 03060 (US). SHEA, Brian: 192 Roosevelt  
Avenue, Norwood, MA 02062 (US).

(21) International Application Number: PCT/US00/17651

(22) International Filing Date: 27 June 2000 (27.06.2000)

(74) Agent: ZHANG, Yin, P.: Testa, Hurwitz & Thibault,  
LLP, High Street Tower, 125 High Street, Boston, MA  
02110 (US).

(25) Filing Language: English

(81) Designated States (national): IN, JP.

(26) Publication Language: English

(84) Designated States (regional): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE).

(30) Priority Data:  
09/347,615 2 July 1999 (02.07.1999) US

Published:

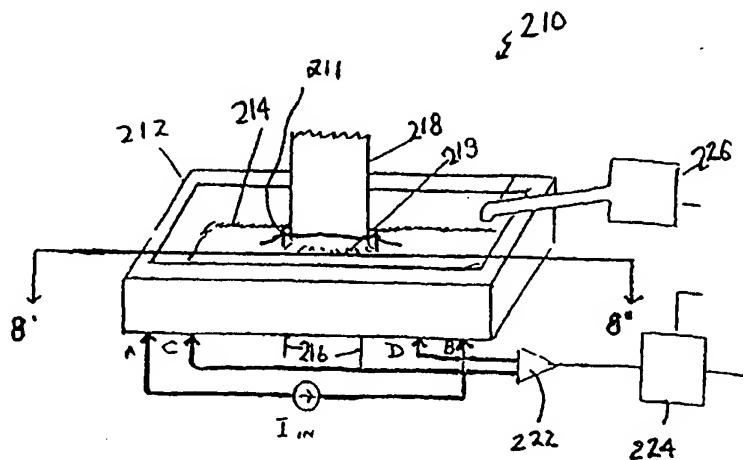
— Without international search report and to be republished  
upon receipt of that report.

(71) Applicant: EVERGREEN SOLAR, INC. [US/US]: 211  
Second Avenue, Waltham, MA 02451 (US).

(72) Inventors: JANOCH, Robert, E., Jr.: 25 Old Homestead  
Road, Westford, MA 01186 (US). GABAREE, Eric,  
Bruce: 2 Fernwood Drive, Milford, NH 03055 (US).

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: EDGE MENISCUS CONTROL OF CRYSTALLINE RIBBON GROWTH



(57) Abstract: An apparatus for growing a crystalline ribbon includes a crucible for holding a melt of a semiconductor material, a pair of strings passing through a pair of openings in the crucible, and a meniscus controller. The pair of strings defines edges of the crystalline ribbon grown from the melt. The crystalline ribbon and an upper surface of the melt form a meniscus. The meniscus controller controls a property of the meniscus near the edges of the crystalline ribbon.

WO 01/04388 A2

## EDGE MENISCUS CONTROL OF CRYSTALLINE RIBBON GROWTH

### Government Support

Work described herein was supported by Federal Grant No. ZAX-8-17647-07, awarded by the Department of Energy. The government has certain rights in the invention.

### 5 Field of the Invention

The invention relates generally to crystal growth, more specifically to ribbon crystal growth.

### Background of the Invention

In order to produce lower cost solar cells and, hence, open up large-scale electrical  
10 applications of solar electricity, it is important to have lower cost substrate materials for making solar cell. A preferred method for achieving this, in the case of crystalline silicon, is through the growth of silicon ribbon in a continuous process as shown in U.S. Patents Nos. 4,661,200; 4,627,887; 4,689,109; and 4,594,229.

Continuous silicon ribbon, in this case, is formed by introducing two high temperature  
15 material strings up through a crucible that contains a shallow layer of molten silicon. The strings serve to stabilize the edges of the growing ribbon and the molten silicon freezes into a solid ribbon just above the molten layer. The molten layer that forms between the strings and the growing ribbon is defined by the meniscus of the molten silicon. The height of this meniscus is about 7mm along the width of the ribbon, which is the height the meniscus would assume  
20 contacting an infinite vertical plane of silicon. At the edges of the ribbon, the radius of curvature of the edge itself causes the meniscus to locally assume a much smaller height, in many cases

- 2 -

causing the meniscus to shrink to less than 5% of its height at the middle of the ribbon. Because there is a thermal gradient from the melt to the growth interface, the reduced meniscus height at the ribbon edges causes more heat to be conducted to the growth interface, resulting in a ribbon that is significantly thinner at the edges than it is in the middle. These thin edges can result in reduced yields during the manufacturing of solar cells on silicon ribbon substrates because the edges are weak and can cause cracks that propagate throughout the substrate.

In addition, the low meniscus at the ribbon edges causes the crystal growth interface to be concave downward. The growth interface, which is concave downward, results in the nucleation of many high angle grain boundaries at the ribbon edges that then tend to grow toward the middle of the ribbon for a distance of several millimeters. These high angle grain boundaries can contain defects which can reduce the solar cell efficiencies.

A means of controlling meniscus height at the edges of a growing crystalline ribbon would thereby be very useful in solving these problems. The following invention describes such a technique.

#### 15 Summary of the Invention

The invention features a system and method in which the meniscus height of the edges of crystalline ribbon grown in a continuous process can be varied and controlled. This can be done by means of specially shaped structures which wet the melt and are placed near the growing ribbon edges. Control of the meniscus at the ribbon edge can then be affected by the specific design and placement of the structures. In particular, the meniscus at the edge can either be made higher, lower, or the same height as the meniscus along the width of the growing ribbon.

Furthermore, these structures can also have thermal properties such as thermal

- 3 -

conductivity and emissivity that enable them to lose heat more rapidly than the surrounding melt. By losing heat more rapidly, these structures can result in making the ribbon thicker. The combined effect of the heat loss and modified meniscus height is to control the thickness of the edge of the growing ribbon independent of the thickness of the ribbon at its middle. The height of the meniscus along the width of the ribbon defines the shape of the crystal growth interface. The effect of changing the edge meniscus height relative to the mid-ribbon meniscus height is that the crystal growth interface shape can be controlled. By making the interface convex downward the growth direction is generally downward and slightly toward the edges. This allows large crystal grains growing in the middle of the ribbon to propagate toward the edges and dramatically reduce the effect of the small high angle grain boundaries that nucleate near the edges.

In one aspect, the invention features an apparatus for growing a crystalline ribbon. The apparatus includes a crucible, a pair of strings, and a meniscus controller. The crucible holds a melt of a semiconductor material. The crucible has a pair of openings, through which a pair of strings is passed. The pair of strings defines the edges of the crystalline ribbon grown from the melt. The crystalline ribbon and an upper surface of the melt form a meniscus. A meniscus controller controls a property of the meniscus near the edges of the crystalline ribbon.

In one embodiment, the meniscus controller is a structural member located in the crucible adjacent to at least one of the strings. For example, the structural member can comprise at least one pin or a generally cylindrical tube. In another example, the structural member can be oriented substantially perpendicular to the plane of the melt. In another example, the pair of strings comprises a first string and a second string, and the structural member comprises a first structural member placed adjacent to the first string and a second structural member placed

- 4 -

adjacent to the second string. In still another example, the structural member and the upper surface of the melt form a meniscus which affects the shape and height of the meniscus near the edge of the crystalline ribbon. In another embodiment, the meniscus controller comprises a wall of the crucible.

5        In one embodiment, the meniscus controller provides a growth interface that is substantially flat. Alternatively, the meniscus controller provides a growth interface that is substantially convex. In another embodiment, the meniscus controller controls the thickness of the crystalline ribbon. For example, the meniscus controller can provide a crystalline ribbon having a uniform thickness. In still another embodiment, the meniscus controller raises the  
10   height of the meniscus near the edges of the crystalline ribbon.

      In another aspect, the invention features an apparatus for growing a crystalline ribbon. The apparatus includes a crucible for holding the melt of a semiconductor material, a pair of strings passing through a pair of openings in the crucible, and a structural member disposed in the crucible adjacent to at least one of the strings. The pair of strings defines edges of the  
15   crystalline ribbon grown from the melt. The crystalline ribbon and an upper surface of the melt form a meniscus. The structural member, disposed in the crucible adjacent to at least one of the strings, raises the height of the meniscus near the edges of the crystalline ribbon.

      In still another aspect, the invention features a method for growing a crystalline ribbon. A melt of a semiconductor material is provided in a crucible. A seed crystal of the  
20   semiconductor material is placed in the melt. The seed crystal is pulled from the melt between a pair of strings passing through a pair of openings in the crucible, thereby solidifying the melt to form the crystalline ribbon. The crystalline ribbon and the upper surface of the melt form a meniscus. A meniscus controller controls a property of the meniscus near the edges of the

- 5 -

crystalline ribbon.

In one embodiment, a property of the meniscus is controlled using a structural member placed in the melt adjacent to at least one of the pair of strings. For example, the structural member can be at least one pin or a generally cylindrical tube. In another embodiment, a  
5 property of the meniscus is controlled using a wall of the crucible.

In one embodiment, the meniscus height at the ribbon edge can be controlled. For example, the meniscus height at the ribbon edges can be controlled independently of the meniscus height at the middle of the ribbon. By changing the meniscus height at the ribbon edge relative to the meniscus height at the middle of the ribbon, the growth interface can be made  
10 concave, flat, or convex. In another embodiment, the thickness at the ribbon edge can be controlled. For example, the thickness at the ribbon edges can be made thinner, the same, or thicker than the thickness at the middle of the ribbon.

In still another embodiment, the invention features a method for growing a crystalline ribbon. A melt of a semiconductor material is provided in a crucible. A structural member is  
15 provided in the crucible adjacent to at least one of a pair of strings passing through a pair of openings in the crucible. A seed crystal is pulled from the melt between the pair of strings. The melt solidifies to form the crystalline ribbon. The crystalline ribbon and the upper surface of the melt form a meniscus. The height of the meniscus near the edges of the crystalline ribbon is raised.

20 Brief Description of the Drawings

The foregoing and other objects, features and advantages of the present invention, as well as the invention itself, will be more fully understood from the following description of preferred

- 6 -

embodiment, when read together with the accompanying drawings, in which:

Figure 1a shows a perspective view of a crystalline ribbon growth system.

Figure 1b shows a side view of the crystalline ribbon growth system of Figure 1a.

Figure 1c shows a top view of the crystalline ribbon growth system of Figure 1a.

5        Figure 2 shows a perspective view of one embodiment of a crystalline ribbon growth system of the invention.

Figure 3a shows a perspective view of one embodiment of a crystalline ribbon growth system of the invention.

10       Figure 3b shows a perspective view of one embodiment of a crystalline ribbon growth system of the invention.

Figure 3c shows a perspective view of one embodiment of a crystalline ribbon growth system of the invention.

Figure 4 shows a perspective view of one embodiment of a crystalline ribbon growth system of the invention.

15       Figure 5a shows a cross-sectional view of a ribbon crystal grown using the crystalline ribbon growth system of Figure 1a.

Figure 5b shows a cross-sectional view of a ribbon crystal grown using the crystalline ribbon growth system of the present invention.

Figure 6a shows a front view of a ribbon crystal grown using the crystalline ribbon

- 7 -

growth system of Figure 1a.

Figure 6b shows a front view of a ribbon crystal grown using one embodiment of the crystalline ribbon growth system of the present invention.

Figure 6c shows a front view of a ribbon crystal grown using one embodiment of the  
5 crystalline ribbon growth system of the present invention.

Figure 7 is a schematic diagram of one embodiment of a continuous crystal growth system.

Figure 8 is a cross-sectional view of the crystal growth system of Figure 7 cut through line 8'-8'' and showing only the crucible and the melt.

10 Figure 9 is a circuit diagram illustrating the resistance of the crystal growth system of Figures 7 and 8.

Figure 10 shows a portion of a system for continuous ribbon crystal growth.

Figure 11 shows an embodiment of a continuous ribbon crystal growth system.

Figure 12 illustrates the calculation of the cross sectional mass area of a pile of granular  
15 material on a horizontal plane.

#### Detailed Description

Referring to Figures 1a-1c, a ribbon crystal growth system 10 includes a crucible 12, a melt 14 placed in the crucible 12, and a pair of strings 13 passing through the crucible 12. The crucible 12 has a pair of openings (not shown) through which the pair of strings 13 passes  
20 through. The melt 14 solidifies and forms a crystalline ribbon 15, as the ribbon is pulled from the melt 14. The pair of strings 13 stabilizes the edges of the crystalline ribbon 15. A meniscus



- 8 -

18 forms between the surface of the melt 14 and the growth interface 20 of the ribbon 15. The upper surface of the meniscus 18 viewed from the front is substantially concave. The growth takes place from the free surface of the melt, resulting in minimal contact with crucible materials and segregation of impurities. The free surface of the melt refers to its top surface. Segregation of impurities occurs because atoms of trace materials are free to move back to the melt as the ribbon material solidifies, resulting in a crystalline ribbon that is purer than the melt. This effect enables one to utilize lower purity and, therefore, lower cost starting materials, or to produce higher quality crystalline ribbon.

As illustrated in Figures 1b and 1c, the meniscus 18 has a height  $h$  and radius of curvature  $R_1$  and  $R_2$ .  $R_1$  represents the radius of curvature in the vertical plane, and  $R_2$  represents the radius of curvature in the horizontal plane.

The generalized Laplace equation can be used to determine the meniscus shape and height for a given material and geometry based on the following equation:

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \rho g h$$

15

In the equation,  $\Delta p$  is the pressure difference between the melt surface and the height  $h$  in the meniscus,  $\gamma$  is surface tension of the melt,  $\rho$  is density of the melt material,  $g$  is acceleration of gravity, and  $h$  is meniscus height.  $R_1$  and  $R_2$  are the radii of curvature of the meniscus in the vertical and horizontal planes.  $R_1$  and  $R_2$  change with vertical height along the meniscus. By integrating this equation from the melt free surface to the meniscus attachment point, or the upper boundary of the meniscus on the ribbon 15, the meniscus height and shape can be determined.

20

- 9 -

For the meniscus 18 near the middle of the ribbon 15, there is essentially no curvature in the horizontal plane, thus  $1/R_2$  drops out of the equation, and the equation can be solved to get a meniscus height. For example, the meniscus height can be about 7 mm for molten silicon wetting a silicon ribbon, where  $\rho$  is about  $2.3 \text{ gm/cm}^3$ ,  $\gamma$  is about 720 dynes/cm, and  $g$  is about  $980 \text{ cm/s}^2$ . For the meniscus 18 near the edge of the ribbon,  $1/R_2$  is a significant factor, and the resulting meniscus height is smaller. As discussed previously,  $R_1$  and  $R_2$  change with vertical height along the meniscus. At the top of the meniscus,  $R_2$  can be about half the thickness of the ribbon. For example, a silicon ribbon 15 having a thickness of about 0.3 mm, which has been used to grow silicon ribbon for use in solar cell applications, the meniscus height near the edge of the ribbon 15 can be about 0.3 mm. The meniscus height near the edges is significantly smaller than near the center. Figure 1a illustrates the difference in height of the meniscus near the center of the ribbon 15 and the edges of the ribbon 15.

During the ribbon growth process, heat is conducted from the melt 14 to the growth interface 20 and from the growth interface 20 to the ribbon 15. The ribbon 15 then radiates heat to the surrounding environment. In addition, the heat of fusion is released at the growth interface 20 as the molten silicon solidifies. The balance of these heat flows determines the ribbon thickness. At the ribbon edge, a reduced meniscus height causes more heat to be conducted from the melt 14 to the growth interface 20 as the growth interface 20 is closer to the melt 14. In addition, the lower meniscus at the edge brings the growth interface into the hotter thermal environment nearer the melt surface, radiating away less heat. The balance of these heat flows provides thinner edges.

Referring to Figure 2, a ribbon crystal growth system 30 of the present invention includes a crucible 32, a melt 34, a pair of strings 36 passing through a pair of holes in the crucible 32,

- 10 -

and a meniscus controller 38. The crystalline ribbon 40 grows from the melt 34 as substantially described above with reference to Figures 1a-1c. However, the meniscus controller 38 modifies the meniscus 42 formed between the melt 34 and the ribbon 40. In one embodiment, the meniscus controller 38 is a pair of structural members positioned in the crucible 32 adjacent the pair of strings 36. A meniscus 44 forms around each structural member 38 as the melt material wets the surface of the structural member 38. A liquid is said to "wet" a solid if the contact angle between the solid and the liquid, measured through the liquid, lies between  $0^\circ$  and  $90^\circ$ . When the melt material wets the surface of the structural member 38, the melt climbs on the structural member 38. Therefore, the material for the structural members 38 is selected based on the wettability of the melt material to the structural members 38. For example, when growing a silicon ribbon, the material for the structural members can be graphite. Alternatively, the material for the structural members and/or the crucible can include carbon, oxygen, silicon, nitrogen or a compound including any of these elements. The meniscus 44 formed around the structural member 38 superimposes over the meniscus 42 and modifies the height of the meniscus 44 near the ribbon edges, without substantially affecting the meniscus 42 near the center of the ribbon 40. The meniscus height near the edges of the ribbon 40 is raised. As a result, the growth interface 43 is substantially straight or substantially convex. Specific design of these structures, such as shape and size, and placement of the structures can therefore be used to control and to vary the meniscus. For example, the meniscus height near the edges of the ribbon can be made higher, lower, or the same height as the meniscus along the entire width of the ribbon.

In one embodiment, vertical pins 52 provided in the melt 54 function as the meniscus controller as shown in Figure 3a. In this embodiment, for the growth of silicon ribbon, two vertical graphite pins 52a, 52b are placed in blind holes in the bottom of the crucible 59 near

- 11 -

each string 51. The first pin 52a is provided on one side of the ribbon 56, and the second pin 52b is provided on the other side of the ribbon 56. A meniscus forms around each pin 52a, 52b. The meniscus formed around each pin 52a, 52b superimposes over the meniscus 58 formed between the growth interface 60 and the melt 54, and thereby raises the height of the meniscus 58 near the edges of the ribbon 56.

In another embodiment, vertical walls 72, provided in the melt 74, modify the meniscus 76 near the edges of the ribbon 78 as shown in Figure 3b. Each vertical wall 72 is placed near the edges of the ribbon 78 substantially perpendicular to the plane of the ribbon 78. A meniscus 79 forming around each vertical wall 72 superimposes over the meniscus 76 and changes the height of the meniscus 76 near the edges of the ribbon 78. These walls 72 can be machined into the crucible 71, or can be separate pieces that are pinned to blind holes in the bottom of the crucible 71.

In still another embodiment, the ribbon crystal growth system 80 includes a crucible 82 having inner walls 84 which modify the meniscus 86 as shown in Figure 3c. The inner walls 84 are located substantially close to the edges of the ribbon 88, such that a meniscus 89 forming around each inner wall 84 interacts with the meniscus 86 formed between the melt 90 and the ribbon 88 and modifies the meniscus 86 near the edges of the ribbon 88. The meniscus 89 forms around each inner wall 84 as the melt material wets the surface of the inner wall 84.

Referring to Figure 4, the ribbon crystal growth system 100 includes hollow half cylinders 102 placed in the melt 106 near the edges of the ribbon 104. The inner surfaces of the cylinders 102 face toward the ribbon edges and the outer surfaces of the cylinders 102 face away from the ribbon 104. An inner surface of a cylinder 102 substantially surrounds an edge of the ribbon 104. The melt 106 wets the inner surfaces of the cylinders 102 and raises the height of the

- 12 -

meniscus near the edges of the ribbon 104. In this embodiment, a pair of strings 108 passes through the hollow inside portions of the cylinders 102 as illustrated in Figure 4. An advantage of the hollow half cylinders 102 is that the meniscus 103 can rise very high along the inner surface of the cylinders 102. The half cylinders 102 can be prepared by cutting full cylinders in half. Alternatively, full cylinders can be machined to provide an opening along the side of the cylinder, to allow the meniscus to connect from this inner surface of the cylinder to the growing crystalline ribbon.

In addition to increasing the meniscus height near the edges of the ribbon, the meniscus controller can enhance cooling of the melt as the melt solidifies, and thereby provide a thicker ribbon near the edges. The structural members used as the meniscus controller, for example, can radiate heat and directly cool the molten silicon near the ribbon edges because the structural members usually extend above the melt and can be made of a material with an emissivity greater than that of the material for the melt. Therefore, through material selection and size of the meniscus controller, the thickness of the ribbon can be controlled. For example, meniscus controllers made of graphite can be used in growing crystalline silicon ribbon.

Figures 5a and 5b illustrate the differences in the cross sections of silicon ribbon grown with and without the meniscus controller. Figure 5a shows a cross section of a ribbon 120 with no meniscus modification at the edges 122. An edge 122 refers to the region near the string 124. The result is necking near the edges 122 and weaker edges, which can lead to breakage. Figure 5b illustrates significant improvement in the thickness of the ribbon 130 near the edges 132 when the meniscus is modified according to the present invention. Necking near the edges 132 is substantially eliminated, such that the ribbon 130 is less likely to break.

As shown in Figures 6a-6c, the meniscus controller used in the present invention also

- 13 -

controls the shape of the growth interface. The growth interface 140 of a ribbon 142 grown without a meniscus controller is substantially concave, downward facing (i.e., frowning) as illustrated in Figure 6a. Since the crystalline ribbon 142 grows in a direction that is nearly perpendicular to the growth interface 140, the frowning interface 140 results in many crystal  
5 grains that nucleate at the edges and subsequently propagate toward the middle of the ribbon 142. As a result, a substantial amount of grain boundaries 144 can form. By modifying the meniscus near the edges of the ribbon as described herein, the growth interface can be made substantially flat as shown in Figure 6b, or substantially convex and upward facing (i.e., smiling) as illustrated in Figures 6c.

10 Referring to Figure 6c, when the interface 150 is substantially convex, the crystal grains nucleate near the middle of the ribbon 152 and propagate toward the edges 154. Therefore, generally either very large grains or grains consisting of coherent twins grow downward and toward the edges of the ribbon 152. Coherent twin grains have crystal structures that are mirror images of one another. These grains then predominate in the ribbon 152, suppressing the many  
15 high angle grains that nucleate at the edges, resulting in a ribbon with significantly larger crystal grains and reduced high angle grain boundaries as shown in Figure 6c.

The present invention can be used with a ribbon growth system comprising a melt depth control as described in co-owned, pending U.S. Patent Application titled "Melt Depth Control for Semiconductor Materials Grown from a Melt," filed on May 3, 1999, which is incorporated  
20 herein by reference.

Referring to Figures 7 and 8, a continuous ribbon growth system 210 includes a crucible 212 containing a pool of molten silicon ("the melt") 214 and a pair of strings 216 extending through the crucible 212. A meniscus controller 211 is positioned near each string 216. A thin

- 14 -

polycrystalline sheet of silicon 218 is slowly drawn from the melt 214 as the cooler liquid silicon crystallizes at the top of meniscus 219. The strings 216 passing through holes (not shown) in the bottom of the crucible 212 become incorporated in and define the edge boundaries of the crystalline sheet 218. The strings 216 stabilize the edges as the sheet 218 grows. The meniscus controller 211 modifies the meniscus. The surface tension of the silicon prevents leaks through the holes of the crucible 212 where the strings 216 pass through. In the continuous-ribbon growth system 210, the melt 214 and the crucible 212 are housed within an inert-gas filled housing (not shown) to prevent oxidation of the molten silicon. Rollers (not shown) keep the sheet 218 moving vertically as the sheet 218 grows. The crucible 212 remains heated to keep the silicon molten in the melt 214.

The depth of the melt 214 is measured, and this information is provided to the feeder 226 to adjust the rate of introducing silicon into the melt 214 to keep the melt depth constant during the crystal growth. The feeder 226 adds silicon pellets to the melt 214 to compensate for the silicon lost from the melt 214 as the crystalline sheet 218 grows from the melt 214. The depth of the melt 214 is measured by passing an input signal through the crucible 212 and the melt 214, and by measuring an output signal generated in response to the input signal. The output signal indicates the depth of the melt.

In one embodiment, a current  $I_N$  is applied to the combination of the crucible 212 and the melt 214 through a pair of electrodes A and B, and a resultant potential is measured. The resultant potential  $V_{OUT}$  is measured by a differential amplifier 222 through a pair of electrodes C and D, and provides a bulk resistance signal. The resultant potential is fed into the feedback circuitry 224, which generates a control signal for controlling the feed rate of the feeder 226. The feedback circuitry 224 is set up to maintain the resultant voltage at a constant level which

- 15 -

corresponds to a desired melt height. In one embodiment, the pair of electrodes C and D is positioned between the pair of electrodes A and B.

The relationship between the melt depth and the measured output signal responsive to an input signal is described as follows. The present method of depth measurement utilizes unique  
5 properties of semiconductors and a commonly used crucible material (e.g., graphite). For example, at room temperature silicon is normally a semiconductor. However, at its melting point, like other semiconductors, silicon becomes a conductor of electricity almost as conductive as a metal. Graphite is also a conductor of electricity, although conductivity of the molten silicon is greater than that of graphite and therefore dominates when measured in parallel.

10 The conductivity of the silicon melt is directly proportional to the cross-sectional area of the silicon melt. A change in the molten silicon melt depth changes the cross-sectional area of the silicon melt and consequently its conductivity, and conversely its resistance. When an electrical current is passed through both the crucible 212 and the melt 214, by making an electrical connection to two points (i.e., electrodes A and B) on the crucible 212, the melt 214  
15 and the crucible 212 wall form a parallel resistive path. Thus, the electric potential developed in response to the applied current is affected by the depth of the melt 214 in the crucible 212. A voltage measurement taken across two points (i.e., electrodes C and D) on the crucible 212 provides a signal which is representative of the combined resistivity of the melt 214 and the graphite crucible 212, and thus represents the height (or depth) of the melt 214 in the crucible  
20 212. The bulk resistivity of a typical graphite material used for the construction of semiconductor processing crucibles is about one milliohm-centimeter. The bulk resistivity of molten silicon is in the order of twenty (20) times less. Thus, if the area of the crucible section is significantly less than 20 times the area of the section of the typical melt (which is a typical case),



- 16 -

then the molten silicon can be considered to be a "shorting layer" on top of a resistive layer of graphite. The measure then would preferably consider the resistance of the melt since the melt dominates the overall electrical conductance. Figure 9 illustrates a circuit diagram of the continuous ribbon growth system 210 of Figures 7 and 8.

5       The present invention can further be incorporated into the crystal growth system having a continuous melt replenishment as described in co-owned, pending U.S. Patent Application Serial No. 09,304,284, titled "Continuous melt replenishment for crystal growth," filed on May 3, 1999, which is incorporated herein by reference.

Referring to Figures 10 and 11, a continuous ribbon growth system 350 includes a  
10 crucible 343 containing a pool of molten silicon ("the melt") 342 and a pair of strings 344 extending through the crucible 343. A meniscus controller 340 is positioned near each string 344. A thin polycrystalline sheet of silicon 341 is slowly drawn from the melt 342, as the cooler liquid silicon crystallizes at the top of meniscus. The meniscus controller 340 modifies the meniscus near the edges of the ribbon 341. The strings 344 passing through holes (not shown) in  
15 the bottom of the crucible 343 become incorporated in and define the edge boundaries of the crystalline sheet 341. The strings 344 stabilize the edges as the sheet 341 grows. The surface tension of the silicon prevents leaks through the holes of the crucible 343 where the strings 344 pass through. In an actual continuous-crystal-growth apparatus, the melt 342 and the crucible 343 are housed within an inert-gas filled housing (not shown) to prevent oxidation of the molten  
20 silicon. Rollers (not shown) keep the sheet 341 moving vertically as the sheet 341 grows. The crucible 343 remains heated to keep the silicon molten in the melt 342. The crucible 343 also remains stationary.

To provide a continuous crystal growth process, the melt 342 needs to be continuously

- 17 -

replenished as some of the melt 342 is lost by solidifying to form a crystalline ribbon. In one embodiment, a granular source material 335 enters a hopper 312 through a large opening and exits the hopper 312 through a small opening, as shown in Figure 11. The granular source material 335 can have non-uniform sized particles. The source material, for example, can be a semiconductor material. In one embodiment, the source material comprises silicon and a dopant such as boron. The source material 335 exiting the hopper 312 disposes a pile of the source material 335 on a translationally moving belt 334. The pile of the source material 335 has an angle of repose, which is determined by the shape and size distributions of the particles forming the source material 335.

10 Referring to Figure 11, the source material 335 disposed on the moving belt 334 is continuously fed into a crucible 343 comprising a melt of the source material 335 at a pre-determined rate. The source material is introduced into the crucible through a funnel 345 and a tube 347. The tube 347 is positioned inside one end of the crucible 343. In one embodiment, the feed rate is constant. The feed rate is based on the angle of repose of the source material.

15 The volume of the source material is equal to the product of the mass cross-sectional area of the source material and the speed of the moving belt. Figure 12 illustrates the mass cross sectional area. The mass cross sectional area is equal to  $H^2/\tan\alpha + HL$ , where  $\alpha$  is the angle of repose, H is the height, and L is the size of the hopper opening just above the belt. The feed rate can be controlled by the rate of movement of the belt in combination with the angle of repose.

20 The belt, for example, can move at a constant rate and thereby introduce the source material into the crucible at a constant rate. The belt can also move at a rate in the range from 2mm/min to 10mm/min. In still another embodiment, the feed rate is based on the cross sectional area of the source material as it resides on the belt, or on the belt speed.

- 18 -

The use of the angle of repose concept along with a slowly moving belt, as shown in Figures 10, 11 and 12, enables one to transport continuously and very accurately, any desired amount of granular silicon into a crucible containing the melt. The cross-section of material emerging from the narrow orifice is constant due to the constancy of the characteristic angle of repose. With this constant cross-section, the amount of material transported can be varied simply by varying the speed of the belt carrying the granular material. This allows a considerable amount of latitude in choosing the particle size distribution and the particle shape distribution for the silicon feeder material.

The present invention which provides control of the meniscus by varying its shape and/or height, control of the ribbon thickness, greater yield, reduced defects, and other benefits described herein, can be incorporated in other crystalline growth systems and methods as well.

#### Equivalents

While the invention has been particularly shown and described with reference to specific preferred embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

- 19 -

## Claims

- 1 1. An apparatus for growing a crystalline ribbon comprising:
  - 2 a crucible for holding a melt of a semiconductor material, the crucible having a pair of
  - 3 openings;
  - 4 a pair of strings passing through the pair of openings, the pair of strings defining edges of
  - 5 the crystalline ribbon grown from the melt, the crystalline ribbon and an upper surface of the
  - 6 melt forming a meniscus; and
  - 7 a meniscus controller for controlling a property of the meniscus near the edges of the
  - 8 crystalline ribbon.
- 1 2. The apparatus of claim 1 wherein the meniscus controller comprises a structural member
- 2 located in the crucible adjacent at least one of the strings.
- 1 3. The apparatus of claim 2 wherein the structural member comprises at least one pin.
- 1 4. The apparatus of claim 2 wherein the structural member is oriented substantially perpendicular
- 2 to a plane of the melt.
- 1 5. The apparatus of claim 2 wherein the structural member comprises a generally cylindrical
- 2 tube.
- 1 6. The apparatus of claim 2 wherein the meniscus controller provides a growth interface that is
- 2 substantially flat.
- 1 7. The apparatus of claim 2 wherein the meniscus controller provides a growth interface that is
- 2 substantially convex.

- 20 -

1 8. The apparatus of claim 2 wherein the pair of strings comprises a first string and a second  
2 string, and the structural member comprises a first structural member placed adjacent the first  
3 string and a second structural member placed adjacent the second string.

1 9. The apparatus of claim 1 wherein the meniscus controller controls a thickness of the  
2 crystalline ribbon.

1 10. The apparatus of claim 9 wherein the meniscus controller provides a crystalline ribbon  
2 having a uniform thickness.

1 11. The apparatus of claim 1 wherein the meniscus controller comprises a wall of the crucible  
2 substantially perpendicular to a plane of the ribbon.

1 12. The apparatus of claim 1 wherein the meniscus controller raises a height of the meniscus near  
2 the edges of the crystalline ribbon.

1 13. The apparatus of claim 1 wherein the structural member is wettable by the semiconductor  
2 material.

1 14. The apparatus of claim 1 wherein the meniscus controller reduces nucleation at the edges of  
2 the crystalline ribbon.

1 15. The apparatus of claim 2 wherein the structural member and the upper surface of the melt  
2 form a meniscus, which affects the meniscus of the crystalline ribbon.

1 16. The apparatus of claim 2 wherein the structural member comprises at least one of carbon,  
2 oxygen, silicon and nitrogen.

1 17. The apparatus of claim 1 wherein the semiconductor material comprises silicon.

- 21 -

1 18. An apparatus for growing a crystalline ribbon comprising:

2 a crucible for holding a melt of a semiconductor material, the crucible having a pair of  
3 openings;

4 a pair of strings passing through the pair of openings, the pair of strings defining edges of  
5 the crystalline ribbon grown from the melt, the crystalline ribbon and an upper surface of the  
6 melt forming a meniscus; and

7 a structural member disposed in the crucible adjacent at least one of the strings for raising  
8 a height of the meniscus near the edges of the crystalline ribbon.

1 19. A method for growing a crystalline ribbon comprising the steps of:

2 a) providing a melt of a semiconductor material in a crucible;

3 b) placing a seed crystal of the semiconductor material in the melt;

4 c) pulling the seed crystal from the melt between a pair of strings passing through a pair  
5 of openings in the crucible, thereby solidifying the melt to form the crystalline ribbon, the  
6 crystalline ribbon and an upper surface of the melt forming a meniscus; and

7 d) controlling a property of the meniscus near the edges of the crystalline ribbon using a  
8 meniscus controller.

1 20. The method of claim 19 wherein step d) comprises controlling a property of the meniscus  
2 using a structural member placed in the melt adjacent at least one of the pair of strings.

1 21. The method of claim 19 wherein step d) comprises controlling a property of the meniscus  
2 using at least one pin placed in the melt adjacent at least one of the pair of strings.

- 22 -

- 1 22. The method of claim 19 wherein step d) comprises controlling a property of the meniscus  
2 using a structural member placed in the melt adjacent at least one of the strings and substantially  
3 perpendicular to the melt.
- 1 23. The method of claim 19 wherein step d) comprises controlling a property of the meniscus  
2 using a generally cylindrical tube placed in the crucible adjacent at least one of the pair of strings.
- 1 24. The method of claim 19 wherein step d) comprises controlling a shape of the meniscus.
- 1 25. The method of claim 24 wherein controlling the shape of the meniscus comprises providing a  
2 growth interface that is substantially flat.
- 1 26. The method of claim 24 wherein controlling the shape of the meniscus comprises providing a  
2 growth interface that is substantially convex.
- 1 27. The method of claim 19 wherein step d) comprises controlling a property of the meniscus  
2 using a wall of the crucible.
- 1 28. The method of claim 19 wherein step d) comprises controlling a height of the meniscus.
- 1 29. The method of claim 28 wherein step d) comprises raising the height of the meniscus near the  
2 edges of the crystalline ribbon.
- 1 30. The method of claim 19 further comprising step d) controlling a thickness of the crystalline  
2 ribbon.
- 1 31. The method of claim 30 wherein step d) comprises providing a crystalline ribbon having a  
2 uniform thickness by raising a height of the meniscus at the edges of the crystalline ribbon.
- 1 32. The method of claim 20 wherein step d) comprises forming a meniscus with the structural

- 23 -

2 member which interacts with the meniscus of the crystalline ribbon.

1 33. The method of claim 19 wherein step a) comprises providing a melt of silicon in a crucible.

1 34. A method for growing a crystalline ribbon comprising the steps of:

2 a) providing a melt of a semiconductor material in a crucible;

3 b) providing a structural member in the crucible adjacent at least one of a pair of strings  
4 passing through a pair of openings in the crucible;

5 c) placing a seed crystal of the semiconductor material in the melt;

6 d) pulling the seed crystal from the melt between the pair of strings, thereby solidifying  
7 the melt to form the crystalline ribbon, the crystalline ribbon and an upper surface of the melt  
8 forming a meniscus; and

9 e) raising a height of the meniscus near the edges of the crystalline ribbon.



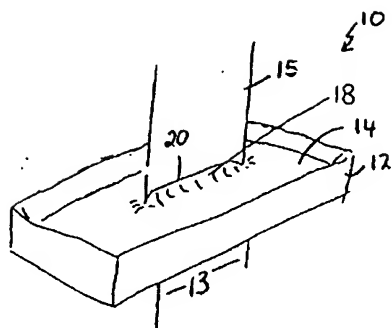


Figure 1a  
(Prior Art)

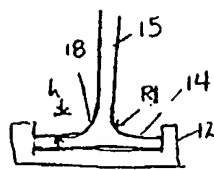


Figure 1b  
(Prior Art)

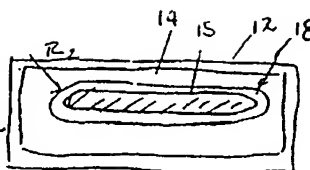


Figure 1c  
(Prior Art)

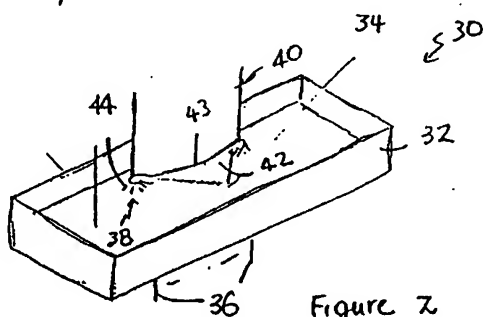


Figure 2

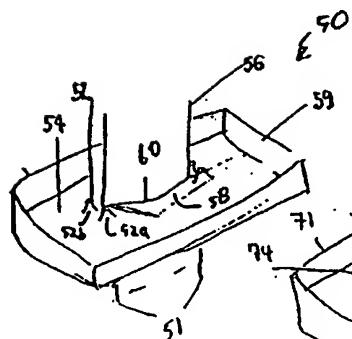


Figure 3a

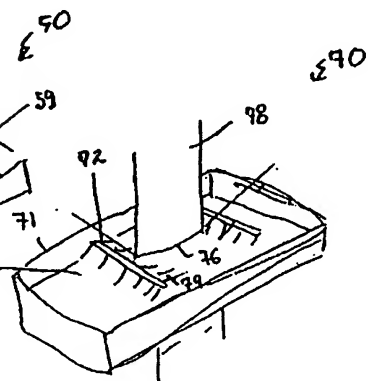


Figure 3b

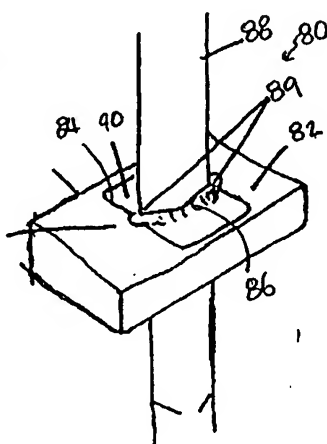


Figure 3c

Figure 4

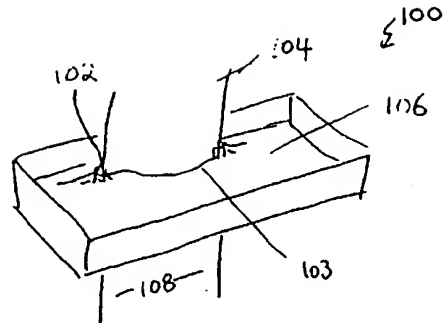


Figure 5

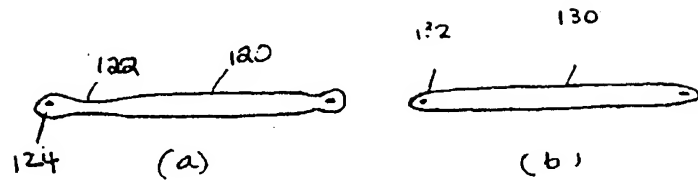


Figure 6

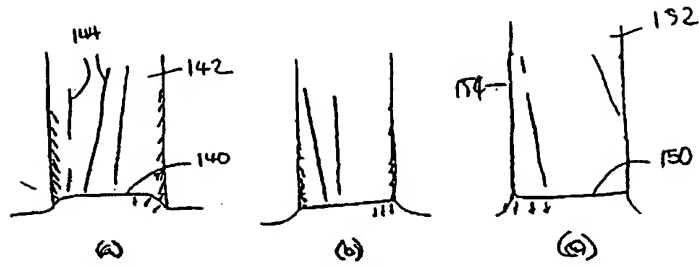


Figure 7

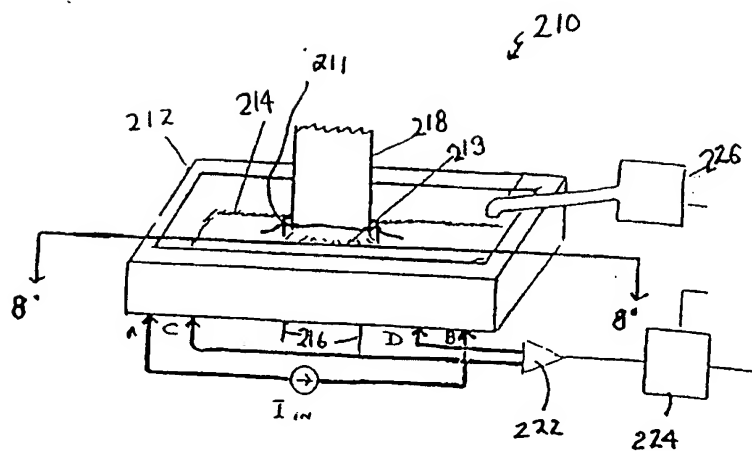


Figure 8

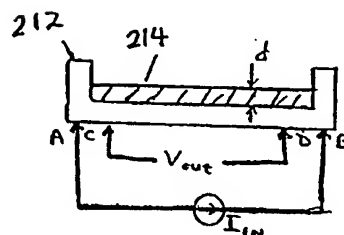


Figure 9

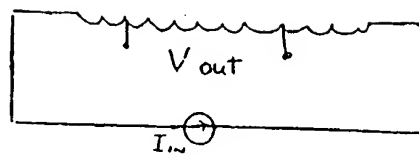


Figure 10

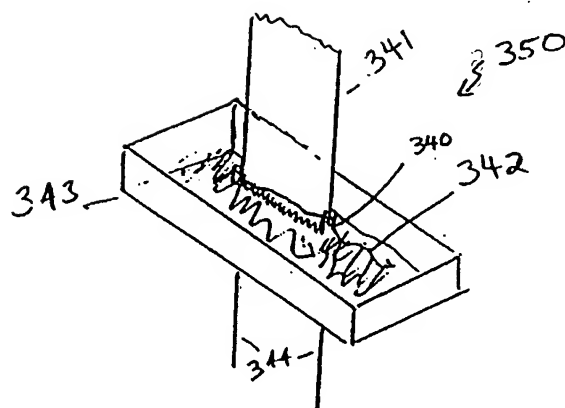


Figure 11

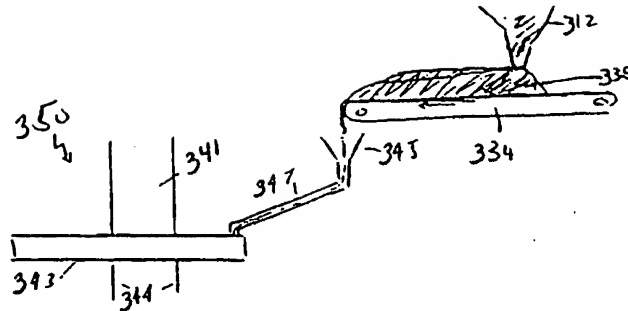
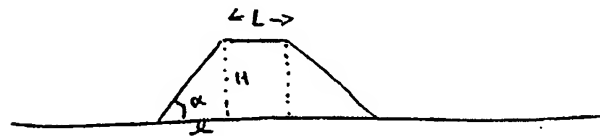


Figure 12



$\alpha \equiv$  angle of repose

$H \equiv$  height

$L \equiv$  horizontal width at bottom of funnel

cross sectional mass area

$$= \frac{1}{2} (H/\tan \alpha) H + \frac{1}{2} (H/\tan \alpha) H + L H$$

$$= H^2/\tan \alpha + L H$$